Studies of the Adsorbing Particle Flotation of Fe^{3+} and Cu^{2+}

Koichi KOBAYASHI,* Kenichi NATORI,** Masamizu KAMAYA,† and Tsunetaka SASAKI††
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo 158

(Received July 29, 1977)

The adsorbing particle flotation of Fe^{2+} or Fe^{3+} and Cu^{2+} ions was studied by the combined use of bentonite (Bt) and a cationic surfactant, benzylhexadecyldimethylammonium chloride (BHDAC). Fe^{3+} ions were effectively floated from an aqueous solution by the use of Bt and cationic surfactant in a manner similar to the flotation by the use of sodium silicate and cationic surfactant. Most Fe^{2+} ions were found to be floated as Fe^{3+} ions, when the pH was increased by the addition of sodium hydroxide. The maximum floatability of 98% was obtained for Fe^{3+} under optimum conditions. The pH corresponding to the beginning of flotation of Fe^{3+} was influenced by the manner in which the pH of the solution was controlled. Cu^{2+} ions could also be floated, but less effectively than Fe^{3+} ions. Selective flotation of Fe^{3+} from the mixed solution of Fe^{3+} and Cu^{2+} was attempted and effectively achieved.

A limited number of studies have been reported for Fe^{3+} and Cu^{2+} ion flotation. Rubin and Johnson studied the effect of pH on the precipitation flotation of Fe^{3+} ion using an anionic surfactant, sodium dodecyl sulfate; the results were compared with a calculated precipitation flotation curve.1) Rubin *et al.* found that Fe^{3+} ions were effectively removed from an aqueous solution by the use of sodium dodecyl sulfate.1) They also studied the removal of Fe^{3+} and Cu^{2+} ions by octadecylamine as a function of pH.1) Floatability of Cu^{2+} ions as $Cu_2[Fe(CN)_6]$ or the 8-quinolinol complex has also been reported.2)

In a previous paper, it was reported that Fe^{3+} ions were effectively removed from an aqueous solution by the ion flotation using sodium silicate and a cationic surfactant, and that the floatability is greatly influenced by the order of addition of these reagents.3) We have also reported that various kinds of heavy metal ions were more effectively floated by the combined use of bentonite and cationic surfactant than by the use of an anionic surfactant alone.4)

In this study, therefore, the adsorbing particle flotation of Fe^{2+}, Fe^{3+}, and Cu^{2+} ions has been attempted and the effects of pH, gas-flow time, and the amount of bentonite on the floatability are reported.

Experimental

Materials. Extra-pure grade ammonium iron(II) sulfate and ammonium iron(III) sulfate, obtained from the Wako Pure Chemical Industries, Ltd. were used without further purification. The copper(II) sulfate used was an extra-pure grade $CuSO_4 \cdot 5H_2O$; it was recrystallized from distilled water. The bentonite powder (Bt) used as an ion exchanger was obtained from the Wako Pure Chemical Industries, Ltd.; the fraction passing through a 350-mesh sieve was collected and dried under reduced pressure. The benzylhexadecyldimethylammonium chloride, a product of the Kao Soap Co., Ltd., was recrystallized from acetone and was dried under reduced pressure. All other chemicals used for colorimetric determination were of analytical reagent-grade, except that the carbon tetrachloride and ammonia used were of special grade.

Apparatus and Procedure. The apparatus and method used for flotation measurements were the same as have been described previously.5) The concentrations of Fe^{2+} and Cu^{2+} ions were determined by colorimetric methods as follows.

Iron:6) Five cm^3 of the solution after flotation was transferred into a 25 cm^3 flask, 0.2 to 0.5 cm^3 of 0.5 mol/dm^3 H_2SO_4 was added to dissolve iron hydroxide, and 2 cm^3 of acetate buffer solution and 1 cm^3 of a 10% solution of hydroxylammonium chloride were added to insure the complete reduction of Fe^{3+} to Fe^{2+} ions. Further, 1 cm^3 of a 0.2% aqueous solution of 1, 10-phenanthroline solution was added to develop the color. After 30 min, the total volume was increased with water to 25 cm^3. The concentration of Fe^{2+} ions was then determined by the colorimeter, Bausch & Lomb, Spectronic 20, at 510 nm. The errors in the colorimetric method due to the scattering of light by Bt are of the order of $\pm 2\%$; this was taken into account by the blank experiment.

Copper:7) 2 to 3 cm^3 of sample solution were transferred into a separatory funnel together with a little water. To this solution were added 5 cm^3 of 20% aqueous solution of ammonium citrate and 2—3 drops of Tymol Blue solution. The mixed solution was adjusted to pH 9.0—9.2 with ammonia, and the total volume was then made 50 cm^3 with water. To this solution was added 1 cm^3 of 1% aqueous solution of sodium diethyldithiocarbamate. The concentration of Cu^{2+} ions extracted in carbon tetrachloride solution was determined by using the colorimeter at 440 nm.

A humidified nitrogen gas was bubbled through a sintered glass plate (No. 4) at the gas-flow rate of 10 cm^3/min. The measurements were conducted at the room temperature of about 25 °C. Floatability was expressed as the percentage of the sublate floated.

Results and Discussion

Ion Flotation of Fe. Floatability and Gas-flow Time: Figure 1 shows the effects of gas-flow time on floatability for the solution containing 1.8×10^{-4} mol/dm^3 Fe^{2+} (which floated as Fe^{3+} ions, as will be mentioned later), 5.0×10^{-5} mol/dm^3 BHDAC, and $1.0 \times 10^{-2}\%$ Bt at the optimum floatability of pH=10.7. It can be seen that the floatability attains a steady value after 1.5 min. Accordingly, all subsequent experiments were made at a gas-flow rate of 10 cm^3/min and a gas-flow time of 2 min

---

* Present address: Laboratory of Chemistry, Musashi Institute of Technology, 1-28-1, Tamatsutsumi, Setagaya, Tokyo 158.

** Present address: Kao Soap Co., Ltd., 1-1, Kayaba-cho, Nihonbashi, Chuo-ku, Tokyo 103.

† Present address: Asahi Kasei Co., Ltd., Yako, Kawasaki-ku, Kawasaki, Kanagawa 210.

†† Present address: Department of Chemistry, Faculty of Science, Tokai University, Hiratsuka, Kanagawa 259-12.

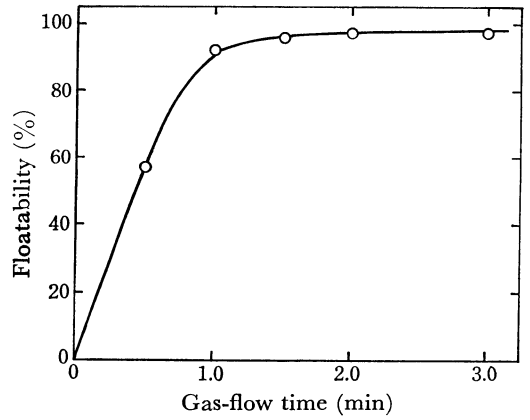

Fig. 1. Effect of gas-flow time on Fe^{3+} floatability.
Fe^{3+}: 1.8×10^{-4} mol/dm^3, BHDAC: 5.0×10^{-5} mol/dm^3, Bt: 1.0×10^{-2}%, pH: 10.7.

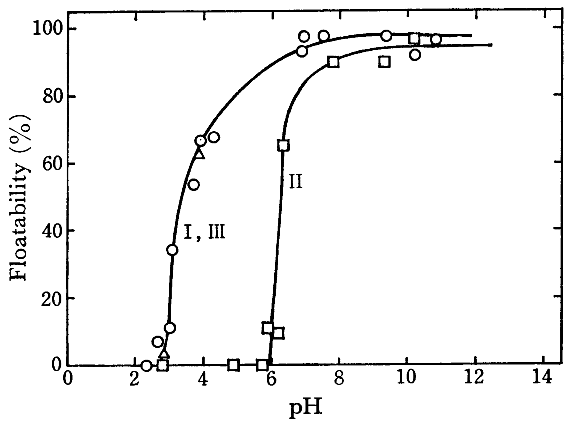

Fig. 2. Effect of pH on Fe^{3+} floatability.
Fe^{2+}: 1.8×10^{-4} mol/dm^3, BHDAC: 5.0×10^{-5} mol/dm^3, Bt: 1.0×10^{-2}%, gas-flow time: 2 min.
I, ○: Aqueous solution prepared by dissolving ammonium iron(II) sulfate in dilute sulfuric acid (pH 2.3) and increasing pH by NaOH.
II, □: Aqueous solution prepared by dissolving ammonium iron(II) sulfate in distilled water (pH 5.7) and increasing pH by NaOH decreasing pH by H_2SO_4.
III, △: Aqueous solution prepared by dissolving ammonium iron(II) sulfate in distilled water(pH 5.7), adjusting pH 2 by H_2SO_4, and raising pH by NaOH.

unless stated otherwise.

Floatability and pH: In order to study the effect of pH on floatability, the flotation was carried out under the conditions of 1.8×10^{-4} mol/dm^3 Fe^{2+}, 5.0×10^{-5} mol/dm^3 BHDAC and 1.0×10^{-2}% Bt. This composition of flotation agents is modeled on the optimum composition of Co^{2+} ion flotation mentioned in a preceding paper.[8] The results are shown in Fig. 2. In Fig. 2, the circles (system I) show the floatability of Fe^{2+} ions from aqueous solutions of varying pH, which were obtained by dissolving ammonium iron(II) sulfate in an aqueous sulfuric acid at pH 2.3 and then increasing the pH by adding sodium hydroxide. The squares (system II) show the floatability of Fe^{2+} ions from an aqueous solution prepared by dissolving ammonium iron(II) sulfate in distilled water of pH 5.7 and adjusting the pH by sodium hydroxide for higher pH and sulfuric acid for lower pH. The triangles (system III) show the floatability of Fe^{2+} ions from an aqueous solution prepared by dissolving ammonium iron(II) sulfate in distilled water of pH 5.7, followed by decreasing the pH to 2 by sulfuric acid and then increasing the pH by the addition of sodium hydroxide.

In the case of systems I and III, the floatabilities increase sharply at pH 3, and reach 95% at pH 6 and above; in the case of system II, the floatability increases sharply by the slight addition of sodium hydroxide only from pH 6 and reaches 95% at pH 8 and above. Generally, metal ions are known to be floated effectively from a solution whose pH value corresponds to the beginning of metal hydroxide formation.[1] However, the present results show that the pH corresponding to the beginning of flotation is influenced by the reagent to be used for the pH control.

In order to clarify the state of the iron ions floated, the amount of Fe^{3+} ions in the sample solution was determined by the chelate titration method using EDTA.[9] The results show that the aqueous solution(I) contains 11% Fe^{3+} ions at pH 2.3, but that the aqueous solution(III), whose pH was decreased below 3 by H_2SO_4 and then increased above 3 by the addition of sodium hydroxide solution, contains 98% Fe^{3+} ions. It was also observed that the precipitate became reddish-brown at pH 3 and above by the addition of sodium hydroxide in the case of systems I and III and above pH 5.7 in the case of system II. In the case of Fe^{3+} solution using ammonium iron(III) sulfate, the floatability curve was the same as that of the systems I and III. Therefore, in the case of systems I and III, Fe^{2+} ions in ammonium iron(II) sulfate solution are considered to be oxidized almost completely to Fe^{3+} ions, as is mentioned in the literature.[10] In the case of system II, the flotation does not occur and the color of the solution does not change to reddish-brown in the pH region of 5.7 and 3. In this pH range for the conditions II, the solution is considered to be in a state of Fe^{2+} ions. Thus the beginning of the flotation and probably the formation of iron(III) hydroxide seems to

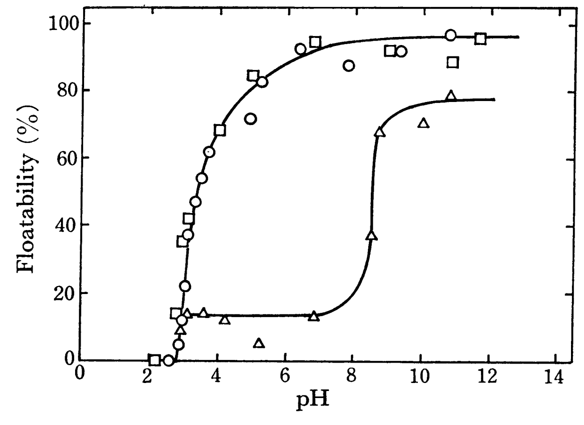

Fig. 3. Effect of pH on Fe^{3+} floatability.
Fe^{3+}: 1.8×10^{-4} mol/dm^3,
△; BHDAC: 5.0×10^{-5} mol/dm^3, gas-flow time: 2 min,
○; BHDAC: 1.0×10^{-4} mol/dm^3, gas-flow time: 7 min,
□; BHDAC: 5.0×10^{-5} mol/dm^3, gas-flow time: 2 min,
Bt: 1.0×10^{-2}%.

be influenced at least by the addition of sodium hydroxide, the reagent used for controlling pH. The reason is not clear at present.

Effect of Bentonite: In order to study the effect of Bt on Fe^{3+} ion flotation, the flotation was carried out at various pH values with and without Bt addition. The results are shown in Fig. 3. As may be seen in Fig. 3, in the system without Bt addition the floatability for the case of gas-flow time of 2 min shows a plateau of 14% in the pH region of 3 to 8, above which it sharply increases. But in the case of the system with Bt addition, as has been shown, the floatability increases sharply at about pH 3; this is shown by the squares in the figure. A marked effect of Bt addition is evident from these curves. Here the Bt acts as a bridge between positively charged iron(III) hydroxide and BHDAC, especially in the relatively low pH region. The rather rapid increase of floatability in a strongly alkaline region in the case of the system without the Bt addition in Fig. 3 may be explained by the interaction between negatively charged iron(III) hydroxide and positive BHDAC ions, as has been reported.[11] It should be mentioned, however, that when the gas-flow time is increased to 7 min, the floatability of the above system without the Bt addition is found to increase and the floatability curve coincides with that of the system I of Fig. 2, as shown by the circles in Fig. 3. The reason for this is not certain, but it is perhaps due to the flotation caused by the weak interaction between similarly charged iron(III) hydroxide and BHDAC, aided by the prolonged gas-flow time.

We have also studied in detail the flotation behavior in the relatively high pH region, and obtained the floatability of Fe^{3+} in a solution of fixed BHDAC concentration at pH 11 as a function of Bt amount added. The results are shown in Fig. 4. In Fig. 4, the floatability decreases for system I with increasing Bt concentration. The decrease of floatability is due to the uptake of BHDAC by Bt, resulting in the decomposition of the Fe hydroxide–BHDAC complex which is effective in the flotation process. In the case of systems II, III, and IV, the floatability increases with increasing addition of BHDAC. In these systems, the presence of a sufficient amount of BHDAC ensures the flotation of negatively charged Fe-hydroxide in the presence of Bt by a mechanism similar to the flotation of permanganate anions reported in an earlier paper.[3]

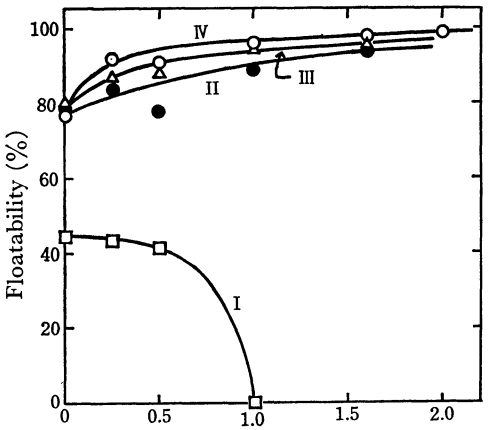

Fig. 4. Effect of Bt on Fe^{3+} floatability.
Fe^{3+}: 1.8×10^{-4} mol/dm^3, gas-flow time: 2 min,
I, □; BHDAC: 2.5×10^{-5} mol/dm^3, pH: 10.9,
II, ●; BHDAC: 5.0×10^{-5} mol/dm^3, pH: 10.9,
III, △; BHDAC: 7.5×10^{-5} mol/dm^3, pH: 10.9,
IV, ○; BHDAC: 1.0×10^{-4} mol/dm^3, pH: 11.7.

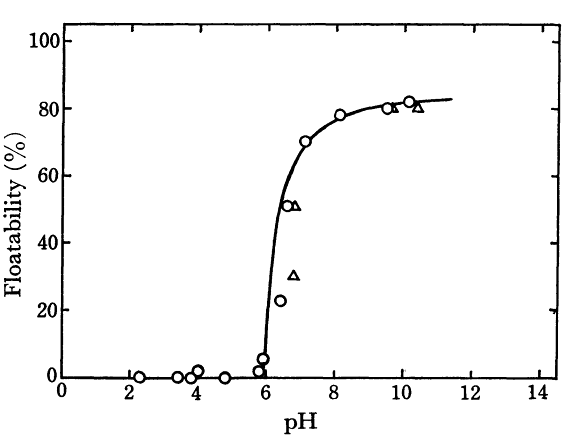

Fig. 5. Effect of pH on Cu^{2+} floatability.
Cu^{2+}: 2.0×10^{-4} mol/dm^3, BHDAC: 5.0×10^{-5} mol/dm^3, gas-flow time: 2 min, ○: 1.0×10^{-2}% Bt, △: 0.5×10^{-2}% Bt.

Ion Flotation of Cu. *Floatability and pH*: The effect of pH on the floatability of Cu^{2+} ions was also measured under conditions of 2.0×10^{-4} mol/dm^3 Cu^{2+}, 5.0×10^{-5} mol/dm^3 BHDAC, and 1.0 or 0.5×10^{-2}% Bt. The results are shown in Fig. 5. It can be seen in this figure that the floatability sharply increases from zero above pH 6; this corresponds to the beginning of Cu(OH)$_2$ precipitation. The increase of the amount of Bt added has little effect, as seen by the comparison of the systems of circles and triangles in the figure. The maximum flotation obtained is not so large as that for the Fe^{3+} ions.

Effect of Bentonite: In order to study the effect of Bt, the flotation was carried out for the system without the addition of Bt and a comparison was made. The results are shown in Fig. 6, together with the system with Bt

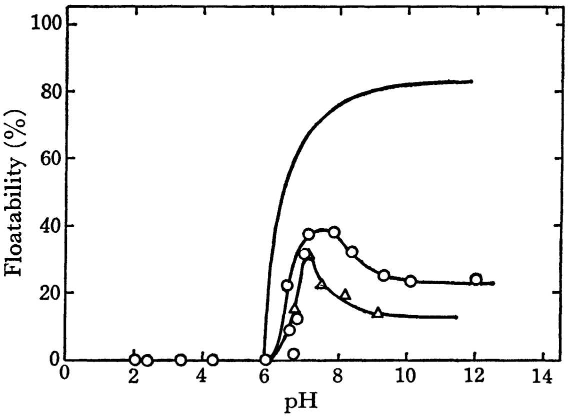

Fig. 6. Effect of pH on Cu^{2+} floatability.
Cu^{2+}: 2.0×10^{-4} mol/dm^3, BHDAC: 5.0×10^{-5} mol/dm^3, gas-flow time (○: 7 min, △: 5 min).
The solid line shows the floatability of Cu^{2+} ions from Fig. 5.

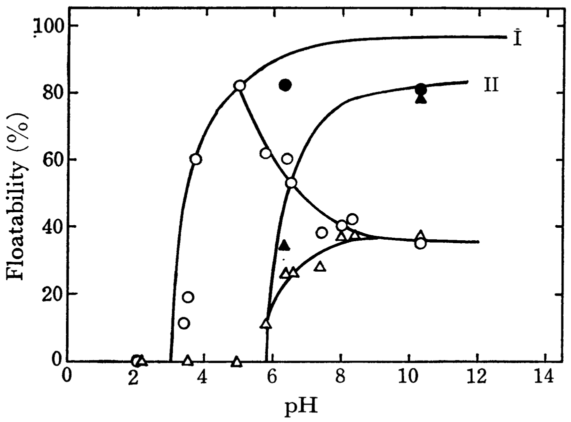

Fig. 7. Selective flotation of Fe^{3+} and Cu^{2+} ions.
Fe^{3+}: 2.0×10^{-4} mol/dm^3, Cu^{2+}: 2.0×10^{-4} mol/dm^3, gas-flow time: 2 min.
BHDAC: 5.0×10^{-5} mol/dm^3, Bt: 1.0×10^{-2}% $\}$ Fe^{3+}(○), Cu^{2+}(△)
BHDAC: 1.0×10^{-4} mol/dm^3, Bt: 2.0×10^{-2}% $\}$ Fe^{3+}(●), Cu^{2+}(▲)
Solid line I: simple system of Fe^{3+} ions.
Solid line II: simple system of Cu^{2+} ions.

(Fig. 5). It is seen in this figure that the lack of Bt remarkably decreases the floatability of Cu^{2+}, and the increase of gas-flow time from 2 min through 5 to 7 min increases the floatability in a slightly different way from the case of Fe^{3+} flotation. The increase of BHDAC concentration shows no effect. Thus, the addition of Bt is found effective in both the reduction of gas-flow time and the increase of floatability.

Selective Ion Flotation from a Mixed System. The flotation of Cu^{2+} and Fe^{3+} ions from a solution containing 2.0×10^{-4} mol/dm^3 Cu^{2+}, 2.0×10^{-4} mol/dm^3 Fe^{3+}, 1.0×10^{-2}% Bt, and 5.0×10^{-5} mol/dm^3 BHDAC was carried out by controlling pH with NaOH. The results are shown in Fig. 7, as open circles and triangles respectively, together with the results obtained for the separate systems of Cu^{2+} and Fe^{3+} ions, shown as solid lines. In the mixed systems, Fe^{3+} and Cu^{2+} ions are floated above pH 3 and 6 respectively, as in the flotations of the separate systems. Thus, even in the mixed system the flotation begins at the point of the formation of insoluble iron and copper hydroxides. Accordingly, the selective flotation of Fe^{3+} ions was achieved between pH 3 and 6, enabling the separation of Fe^{3+} ions from Cu^{2+} ions. However, in the above system, because of a relatively limited amount of Bt and BHDAC, the floatability of Fe^{3+} ions decreases as soon as the Cu^{2+} ion flotation begins and they both attain a steady value of about 40% at pH values higher than 8. In the case of a sufficient addition of Bt and BHDAC, as shown by the solid curves and triangles in Fig. 7, the flotation of Fe^{3+} and Cu^{2+} ions increases; beyond pH 10, the flotation of both Fe^{3+} and Cu^{2+} attains their steady maximum of about 80%. These conditions are applicable for the non-selective removal of both Fe^{3+} and Cu^{2+}.

References

1) A. J. Rubin and J. D. Johnson, *Anal. Chem.*, **39**, 298 (1967).

2) B. M. Davis and F. Sebba, *J. Appl. Chem.*, **17**, 41 (1967); E. J. Mahne and T. A. Pinhold, *Chem. Ind. (London)*, **30**, 1299 (1966).

3) I. Takayanagi, K. Kobayashi, K. Hachisuka, and T. Sasaki, *Bull. Chem. Soc. Jpn.*, **49**, 2419 (1976).

4) K. Kobayashi, *Bull. Chem. Soc. Jpn.*, **48**, 1750 (1975); K. Kobayashi, H. Sato, K. Kachi, M. Nakamura, and T. Sasaki, *ibid.*, **48**, 3533 (1975); K. Kobayashi, N. Watabe, and T. Sasaki, *ibid.*, **49**, 2701 (1976).

5) K. Kobayashi, *Bull. Chem. Soc. Jpn.*, **48**, 1180 (1975).

6) F. Snell and C. Snell, "Colorimetric Methods of Analysis," C. Van Nostrand Company, New Jersey (1948), p. 314.

7) F. Snell and C. Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Company, New Jersey (1948), p. 111.

8) K. Kobayashi, H. Sato, K. Kachi, M. Nakamura, and T. Sasaki, *Bull. Chem. Soc. Jpn.*, **48**, 3533 (1975).

9) K. Sugahara and T. Michino, "Teiryobunseki," Asakura Co., Tokyo (1962), p. 101.

10) G. Charlot, "L'analyse Qualitative et Les Réactions en Solution," Mason et Cie, Paris (1957).

11) R. B. Grieves and D. Bhattacharyya, *J. Am. Oil Chem. Soc.*, **44**, 498 (1967).